

Experimental-Computational Coupled Kinetic Model for Oxygen Transfer in Catalyst-Metal-oxide System for Chemical Looping Epoxidation

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Highlights

- Selective chemical looping offers a greener approach to ethylene oxide synthesis.
- Coupled kinetic model integrates theoretical screening, TGA, EIS and DFT.
- Derived model guides oxygen carrier selection and reactor design, enhancing ethylene epoxidation.

1. Introduction

Ethylene oxide (EO) is a crucial chemical used in various industrial processes, including disinfection, sterilisation, and the production of antifreeze, polyester fibres, and surfactants. The conventional method of EO production involves mixing oxygen and ethylene with a silver catalyst, but this imposes safety risks, while also emits greenhouse gases and releases volatile organic compounds. To reach the green chemistry targets to drive the future industrial society, alternative approaches are needed. Chemical-looping (CL) selective oxidation was demonstrated promising in synthesising ethylene oxide. Instead of gaseous oxygen, solid particles of metal oxides serve as oxygen donors – termed oxygen carriers. An oxygen carrier is a substance that can reversibly store and release oxygen, preventing direct contact between an oxidised component and oxygen. Unfortunately, the current efficiency of CL-epoxidation is lower than the industrially established technique [1,2]. To boost the performance of CL-epoxidation, the selection of metal oxide that works as an oxygen carrier is a vital factor. The design space for oxide is broad and expanding with experimental and theoretical progress, however, the availability of oxygen from the solid is only one aspect that needs to be considered. Additionally, oxygen transport mechanics within those bulk metal oxides, and on the interface between the catalyst and metal oxides, play a significant role in chemical looping processes, but our understanding of the oxygen pathways remains very limited. The purpose of the current study is to derive an experimental-computational kinetic model for oxygen transfer in the catalyst-metal oxide system to achieve process-tailored CL-materials for competitive CL epoxidation. Conclusions from our mechanistic studies will inform the design of CL-reactors, helping drive the reaction performance towards an industrial application.

2. Methods

We developed a combined computational and experimental methodology to build a kinetic model describing the oxygen transfer regime from the bulk, through the interface between catalyst-metal oxide to the place of heterogeneous reaction, and eventually leaving as ethylene oxide. A preliminary list of candidate metal oxides was selected *via* screening the Materials Project database for materials' ground energies and redox temperatures [3].

The possible candidates were then synthesised experimentally; their structures were identified through X-ray powder diffraction (XRD, Bruker D8 Advance diffractometer), and the results were analysed with Profex to quantify the composition. Thermo-gravimetric analyses (TGA) were taken to characterise materials' thermochemical properties. The TGA experiments were carried out with a TGA/DSC 1, Mettler Toledo. A set of temperature programmed reduction and oxidation runs was operated cyclically, with N₂ for the reduction step and air (21% O₂) for oxidation, and temperature changes from 50°C to 700°C and back. Then, ethylene epoxidation experiments were conducted with the chosen silver catalyst-metal oxides pairs to quantify the total oxygen release to the ultimate product.

Electrochemical impedance spectroscopy (EIS) was employed to study the oxygen diffusion within the bulk and at the interface between the catalyst and metal oxides contact surface. Frequency-dependent

impedance curves were obtained through Biologic VSP 300 potentiostat [4]. Finally, the contribution of the Ag catalyst to the oxygen yield at the interface between the Ag-perovskite was theoretically assessed using Density Functional Theory (DFT), implemented in the CASTEP code [5].

3. Results and discussion

The metal-oxide candidates resulting from the Material Project database screening are presented in Fig. 1-a. As the conventional ethylene epoxidation occurs around 200°C-300°C, to select the promising metal oxides for epoxidation, the upper temperature limit was broadened by 50°C to allow for more candidates. Based on the redox temperature and synthesis methods, the selected oxides for experimental assessment included: BaFeO₃, BaMnO₃, SrFeO₃, YMnO₃, CaFeO₃, MgMnO₃, and SrMnO₃. Preliminary results of TGA with air/nitrogen atmosphere for BaFeO₃ and BaMnO₃ are illustrated in Fig. 1-b. The stabilised 5% mass change of BaFeO₃ occurred around 300°C, while the stabilised 1% mass change of BaMnO₃ started at a lower temperature, about 200°C. Both materials showed certain oxygen mobility and cyclability. The Nyquist plot of SrFeO₃ measured by EIS is shown in Fig. 1-c. The semicircular behaviour in the high frequencies indicated the bulk response from the sample, while the no spike signal in the low frequencies implied that no impedance barrier to charge transfer between the metal electrode and the sample.

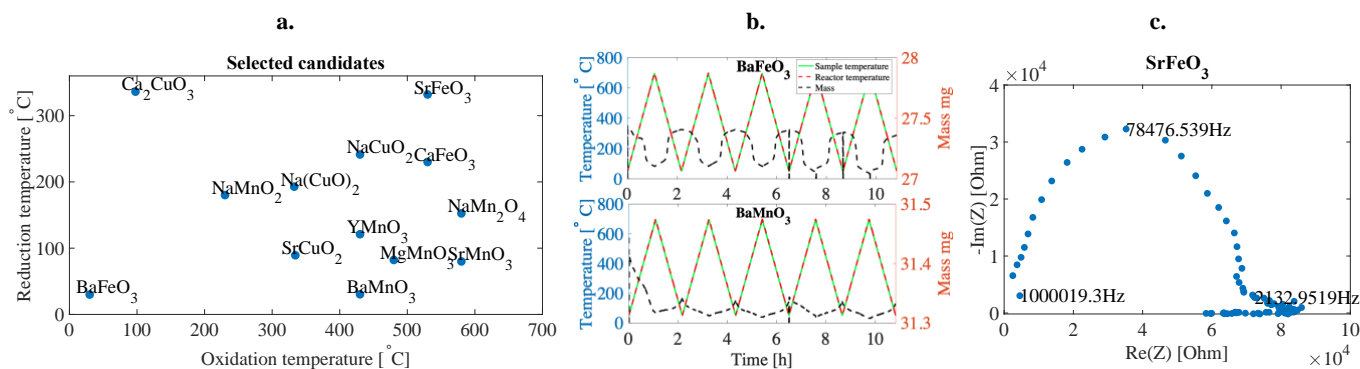


Figure 1. a. Selected metal oxide candidates in terms of redox temperature calculated from the Material Project database. b. Mass change of BaFeO₃ and BaMnO₃ from TGA in the atmosphere of air/nitrogen atmosphere. c. Nyquist plot of SrFeO₃ measured by EIS.

4. Conclusions

This study highlights the potential of CL selective oxidation as a viable alternative for ethylene epoxidation. Theoretical screening from the Material Project database offers us a controllable materials pool to yield promising candidates, BaFeO₃, BaMnO₃, SrFeO₃, YMnO₃, CaFeO₃, MgMnO₃, and SrMnO₃. And the results from TGA validate the oxygen capability of those candidates, BaFeO₃ and BaMnO₃ are demonstrated to reversibly store oxygen at low temperatures. The EIS presents the oxygen diffusion within the bulk material (SrFeO₃). Further DFT calculations quantify the oxygen spill-over at the catalyst-metal oxide interface. Overall, the results contribute to the establishment of an experimental-computational kinetic model for oxygen transfer within the catalyst-metal oxide system.

References

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Keywords

Chemical looping epoxidation; Oxygen transfer; Electrochemical impedance spectroscopy; Density functional theory